

Adsorption of Cu(II) ions on cotton boll

H. Duygu Ozsoy*, Halil Kumbur

Department of Environmental Engineering, Engineering Faculty, Mersin University 33360, Turkey

Received 1 September 2005; received in revised form 18 November 2005; accepted 16 January 2006

Available online 21 February 2006

Abstract

In this study, cotton boll was used as an adsorbent for the aim of removing of the Cu(II) ions from the aqueous solutions. The adsorption process was carried out in a batch process and the effects of contact time (2–24 h), adsorbent concentration (1–20 g l⁻¹), initial pH (2.0–6.0), initial metal ion concentration (20–160 mg l⁻¹) and temperature (20–45 °C) on the adsorption were investigated. Experimental results showed that the maximum adsorption capacity was determined at pH 5.0 and adsorbed Cu(II) ion concentration was increased with increasing adsorbent concentration and contact time. The isothermal data of cotton boll could be well described by the Langmuir equations and the Langmuir monolayer capacity had a mean value of 11.40 mg g⁻¹. Experimental results indicated that the pseudo-second order reaction model provided the best description of the data with a correlation coefficient 0.99 for different initial metal concentrations and therefore it was explained that chemical sorption was the basic mechanism in this system. FT-IR results showed that oxygen and nitrogen atoms in structure of cotton boll were involved in Cu(II) ions adsorption. © 2006 Elsevier B.V. All rights reserved.

Keywords: Adsorption; Cotton boll; Cu(II); Langmuir isotherm model; Pseudo-second order kinetic model

1. Introduction

Heavy metal contamination of various water resources is of great concern because of the toxic effect to the human beings, other animals and environment. The major sources of heavy metal pollutants are usually from many industries and agricultural activities [1]. Copper is known to be commonly used heavy metals. This metal, which find many useful applications in our life, are very harmful if they are discharged into natural water resources and many pose finally a serious health hazard [2].

The toxicity of copper in humans has been comprehensively reviewed by some researchers. Acute copper poisoning after ingestion may show systemic effects such as hemolysis, liver and kidney damage, and fever with influenza syndrome. Local effects reported include irritation of upper respiratory tract, gastrointestinal disturbance with vomiting, and diarrhea and a form of contact dermatitis [3]. Therefore it is necessary to treat copper-containing wastewater before discharging in to water streams.

The commonly used traditional methods for the treatment of metal-contaminated wastewater include chemical precipitation and filtration, chemical oxidation or reduction, electrochemical treatment, reverse osmosis, solvent extraction, ion exchange and evaporation, all show several disadvantages, such as high cost, incomplete metal removal, low selectivity, high energy requirements, the generation of toxic slurries that are difficult to be eliminated [4].

In recent years, there has been considerable interest in the use of biological materials including, algae, bacteria, fungi, agricultural by-products and residues as adsorbents to remove toxic metals from aqueous solution by adsorption since they are cheap and have high efficiency adsorbents for adsorption of pollutants [5–9]. One of the agricultural by-products from waste of cotton factory is cotton boll, which are an abundant, cheap and readily available residue. To our knowledge, they have not been used for heavy metal ions removal from aqueous solutions.

The purpose of the present study was investigate the possible use of cotton boll, which was not used as an adsorbent material before, for removal of Cu(II) ions from aqueous solutions and also determine the effects of contact time, initial pH, initial metal ion concentration, temperature different adsorbent doses on adsorption efficiency and mechanism of the adsorption.

* Corresponding author. Fax: +90 324 361 00 99.

E-mail addresses: ozsoyhd@mersin.edu.tr (H.D. Ozsoy), hkumbur@mersin.edu.tr (H. Kumbur).

2. Materials and methods

2.1. Materials

The cotton boll used in this study were supplied by Cukurova Region, Turkey. Raw cotton boll were washed by about 21 of distilled water and dried in an oven for 24 h at 105 °C. Materials were ground into appropriate particle size by a blender and then screened through a US standard 14 mesh sieve.

2.2. Chemicals

The stock solution of Cu(II) was prepared in 1.0 g l⁻¹ concentration using CuSO₄·5H₂O and then diluted to appropriate concentrations. HNO₃ and NaOH were obtained from Merck and used for pH value adjustment.

2.3. Fourier transform infrared spectroscopy (FT-IR) analysis

FT-IR analysis in the solid phase was performed using a Fourier transform infrared spectrometer (Satellite FT-IR, Mattson). Adsorbent powders was blended with IR-grade KBr in an agate mortar and pressed into tablet. Spectra of the cotton boll before and after Cu(II) sorption were recorded.

2.4. Adsorption experiments

Adsorption studies were performed in 100 ml erlenmeyer flasks by addition of adsorbent to 50 ml of copper solutions. The pH was adjusted with 1 M HNO₃ and 1 M NaOH before the addition of adsorbents. In all experiments, the flasks were shaken at 150 rpm on a shaker. Contact time was 24 h except for the contact time experiments. After shaking, samples were filtered and the final metal concentration of the filtrate was determined by flame atomic absorption spectrometry (Perkin-Elmer AAnalyst 700 Atomic Absorption Spectrophotometer; wavelength: 324.8 nm; slit width: 0.7 nm; lamp current: 30 mA). The same procedure was applied for different amount of adsorbent added to 50 ml of distilled water. They served as a control (blank). All experiments were performed in triplicate.

The amount of adsorbed copper at equilibrium, q_{eq} (mg g⁻¹) and the percent of adsorption (%) were calculated as follows [10]:

$$q_{eq} = \frac{(C_0 - C_{eq})V}{x} \quad (1)$$

$$\text{percent of adsorption (\%)} = \frac{C_0 - C_{eq}}{C_0} \times 100 \quad (2)$$

where C_0 and C_{eq} are the initial and equilibrium concentrations of copper (mg l⁻¹), V the volume of solution (l) and x is the weight of sorbent (g).

2.5. Equilibrium isotherms

The Langmuir isotherm was used to describe observed sorption phenomena. The Langmuir isotherm applies to adsorption on completely homogenous surface with negligible interaction between adsorbed molecules [11,12]. The linear form of the equation can be written as

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{bq_{max}} + \frac{C_{eq}}{q_{max}} \quad (3)$$

where C_{eq} is the equilibrium concentration of copper, q_{eq} the amount of adsorption at equilibrium, q_{max} the mono layer capacity, and b is an equilibrium constant of Langmuir.

The Freundlich isotherm (empirical model adsorption in aqueous systems) was also tested with our experimental data. The linear form of the equation can be written as

$$\ln q_{eq} = \ln K_f + \frac{1}{n} \ln C_{eq} \quad (4)$$

where K_f is the measure of sorption capacity, and $1/n$ is the sorption intensity.

2.6. Kinetics of adsorption

In order to analyse the sorption kinetics of Cu(II) ions, the pseudo-first order and pseudo-second order kinetic models were applied to data. A simple pseudo-first order equation due to Lagergren was used by different researchers [13,14]:

$$\log(q_{eq} - q_t) = \log q_{eq} - \frac{k_{ad}}{2.303t} \quad (5)$$

where q_{eq} and q_t are the amount of adsorption at equilibrium and at time t respectively, and k_{ad} is the rate constant of the pseudo-first order adsorption process. Plot of $\log(q_{eq} - q_t)$ versus t gives a straight line for first order adsorption kinetics, which allow computation of the adsorption rate constant, k_{ad} .

Ho's second-order rate equation which has been called pseudo-second order kinetic expression has also been applied widely [15,16].

The linear form of the kinetic rate equations can be written as follows:

$$\frac{t}{q_t} = \frac{1}{kq_{eq}^2} + \frac{1}{q_{eq}}t \quad (6)$$

where k is the rate constant of sorption (dm³/mg min), q_{eq} the amount of metal ion sorbed at equilibrium (mg g⁻¹), and q_t is the amount of metal ion sorbet at time t (mg g⁻¹). The constants can be determined experimentally by plotting of t/q_t against t .

3. Results and discussion

3.1. The effect of the temperature

The effect of temperature on the Cu(II) ions removal was illustrated in Fig. 1. The maximal adsorption efficiencies (78.3%) were found at 40 °C. While the increasing trend of adsorption was observed with increasing temperature from 20

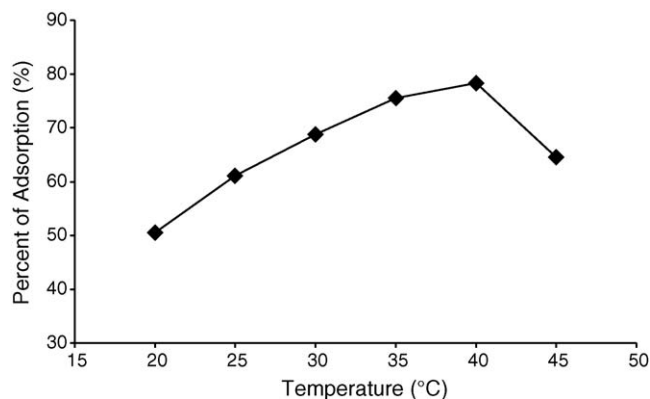


Fig. 1. The effects of temperature on adsorption of Cu(II) ions (100 mg l^{-1}) to the cotton boll (adsorbent dosage, 10 g l^{-1} ; contact time, 24 h; pH 5.0).

to 40°C , adsorption efficiency of cotton boll was decreased with temperatures higher than 40°C . The increase in adsorption capacity of cotton boll with temperature from 20 to 40°C indicates an endothermic process. Meena et al. [17], reported that the increase in adsorption with temperature may be attributed to either increase in the number of active surface sites available for adsorption on the adsorbent or the decrease in the thickness of the boundary layer surrounding the adsorbent with temperature, so that the mass transfer resistance of adsorbate in the boundary layer decreases. The decrease in adsorption capacity of cotton boll at higher temperature (above 40°C) may be attributed to the deactivation of the adsorbent surface or the destruction of some active sites on the adsorbent surface due to bond rupture.

3.2. The effect of the initial pH

Results of the experiments using 100 mg l^{-1} Cu(II) solutions and 10 g l^{-1} adsorbent showed that efficiencies of adsorption were increased with increasing pH from 2.0 to 5.0 (Fig. 2). At low pH values, the surface of adsorbent would also be surrounded by hydronium ions, which decrease the copper interaction with binding sites of the cotton boll by greater repulsive forces. As the pH increased, the overall surface on the cotton

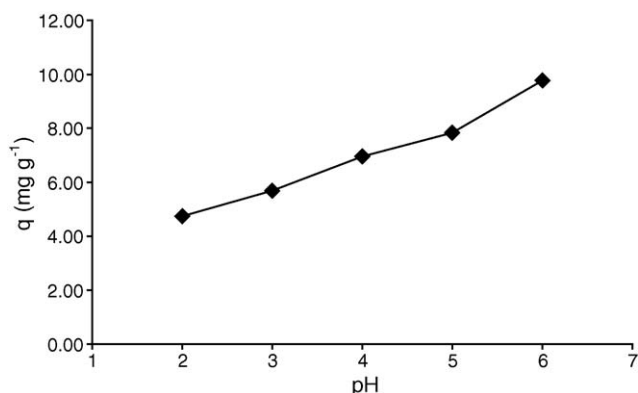


Fig. 2. The effects of the initial pH on adsorption of Cu(II) ions (100 mg l^{-1}) to the cotton boll (adsorbent dosage, 10 g l^{-1} ; contact time, 24 h; 40°C).

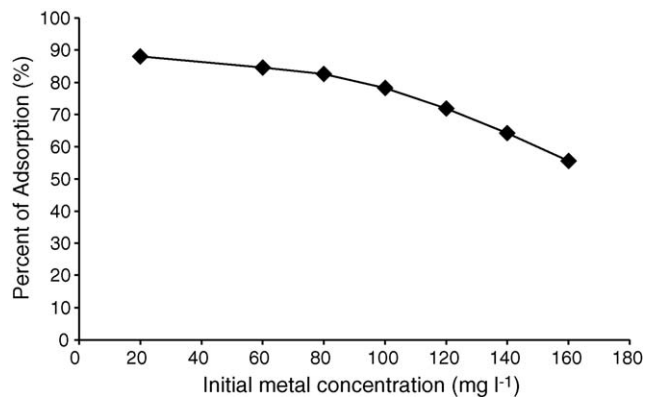


Fig. 3. The effects of the initial Cu(II) ion concentration on adsorption of Cu(II) ions to the cotton boll (adsorbent dosage, 10 g l^{-1} ; contact time, 24 h; 40°C ; pH 5.0).

boll became negative and adsorption increased. At pH values above pH 5.0, turbidity was observed in medium. This can be explained by precipitation of copper ions in the solution. Similarly, some researchers reported that pH has a significant role on Cu removal and the sorption efficiency of Cu(II) was optimal at pH 5.0. They reported also that at pH's above 6.0 Cu(II) ions were precipitated as hydroxides [2,6,18].

3.3. The effect of adsorbent dosage

The removal of the Cu(II) ions from aqueous solutions (100 mg l^{-1}) was significantly depending on the amount of adsorbent. Efficiencies of adsorption were increased (from 29.4 to 78.3%) with increasing of the amount of adsorbent from 1 to 10 g l^{-1} (contact time 24 h; 40°C ; pH 5.0). Similarly, Ozer et al. [10] reported that the increase in adsorbent (dehydrated wheat bran) dosage from 0.5 to 6.0 g l^{-1} resulted in an increase from 21.5 to 97.5% in adsorption of Cu(II) ions. The reason for that is the availability of more binding sites for complexation of Cu(II) ions.

3.4. The effect of the initial Cu(II) ion concentration

The adsorption of Cu(II) by cotton boll was studied at different Cu(II) ion concentrations in the range from 20 to 160 mg l^{-1} . Results are presented in Fig. 3. Although percent of adsorption (%) decreased, equilibrium sorption capacity of cotton boll increased with increasing initial Cu(II) ion concentration. The initial concentration provides an important driving force to overcome all mass transfer resistance of Cu(II) ions between the aqueous and solid phases, hence a higher initial concentration of Cu(II) ions may increase the adsorption capacity. Similarly, Hanzlik et al. [7] showed that adsorption of Cu(II) ions increased as a function of increasing Cu(II) concentration. Ozer et al. [10] indicated that at lower concentrations, all Cu(II) ions present in solution could interact with the binding sites and thus the percentage adsorption were higher than those at higher initial Cu(II) ion concentrations. At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites.

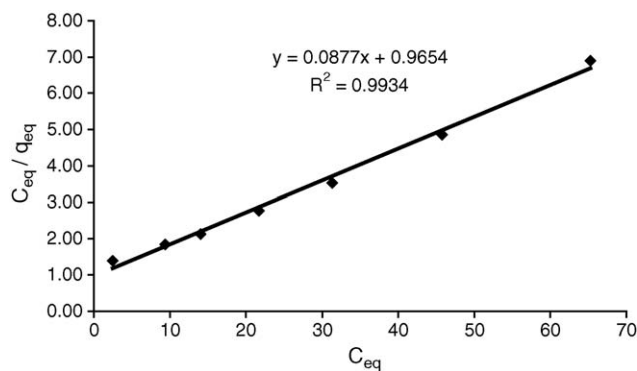


Fig. 4. The Langmuir adsorption isotherms for Cu(II) adsorption by cotton boll (adsorbent dosage, 10 g l^{-1} ; pH 5.0; initial metal concentration of $20\text{--}160 \text{ mg l}^{-1}$; 40°C).

3.5. Adsorption isotherms

In order to investigate the sorption isotherm for cotton boll, two equilibrium models were employed: the Langmuir and Freundlich isotherm equations.

The adsorption constants of Freundlich isotherms K_f and n were estimated from the intercept and slope of $\ln q_{\text{eq}}$ versus $\ln C_{\text{eq}}$, according to Eq. (4) and obtained as 1.39 and 1.93, respectively. The correlation coefficient of Freundlich isotherm (R^2) was 0.9104.

In this study Langmuir model was the best-fit isotherm for adsorption of Cu(II) to the cotton boll. Langmuir isotherm model parameters, q_{max} and b , were estimated from the intercept and slope of $C_{\text{eq}}/q_{\text{eq}}$ versus C_{eq} , according to Eq. (3) and obtained as 11.4 mg g^{-1} and 0.09 l g^{-1} , respectively. The correlation coefficient of Langmuir isotherm (R^2) was 0.9934 (Fig. 4).

A comparison of the maximum capacity, q_{max} , of cotton boll with those of some other adsorbents reported in literature is given in Table 1. It shows that cotton boll has good adsorption capacity when compared with other adsorbents. The adsorption capacity differences of metal uptake are due to the properties of

Table 1
A number of adsorbents available for adsorption of Cu(II) ions

Adsorbent	q_{max} (mg g^{-1})	Reference
Dead fungal biomass (<i>Schizophyllum commune</i>)	1.52	[23]
Sawdust	1.79	[12]
Baggase fly ash	2.26	[20]
Peanut hulls	2.95	[5]
Dead fungal biomass (<i>Pleurotus pulmonarius</i>)	6.20	[23]
Wheat shell	8.34	[18]
Pine bark	9.47	[19]
Tree fern	10.6	[21]
Cotton boll	11.40	Present study
Sphagnum moss peat	12.4	[16]
Activated carbon (Filtrisorb 200)	24.1	[22]
Dehydrated wheat bran	51.51	[10]

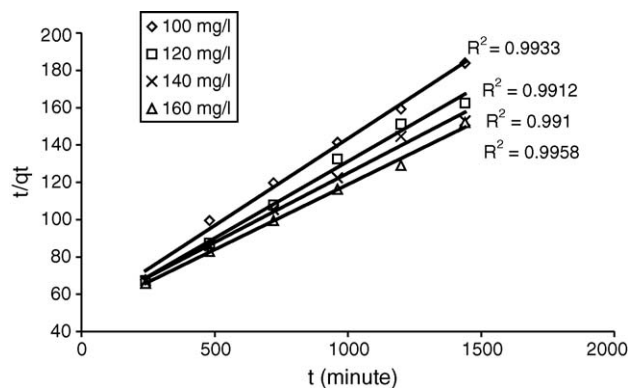


Fig. 5. The plots of pseudo-second order kinetics with respect to different initial metal concentrations (adsorbent dosage, 10 g l^{-1} ; pH 5.0; 40°C).

each adsorbent such as structure, functional groups and surface area.

3.6. Kinetics of adsorption

The efficiency of adsorption was increased with increasing contact time from 2 to 24 h. The blank samples were below the limit of detection 0.077 mg l^{-1} .

The kinetics of Cu(II) ions adsorption on cotton boll was studied with respect to different initial metal concentrations. Experimental results indicated that the pseudo-second order reaction model provided the best description of the data with a correlation coefficient 0.99 for different initial metal concentrations (Fig. 5).

The values, which were derived for the reaction rate constant for pseudo-first and pseudo-second order equations, are shown at Table 2. The results indicated that the adsorption system studied follows to the pseudo-second order kinetic model at all time intervals and pseudo-second order rate constants were affected by initial Cu(II) ions concentration and chemical sorption was the basic mechanism in this system.

3.7. Adsorption mechanisms

Kinetic results of adsorption indicated that chemical sorption was the basic mechanism in this system. Cotton boll is a complex material containing lignin and cellulose as major constituents. Therefore chemical sorption may occur by the polar functional groups of lignin, which include alcohols, aldehydes, ketones, acids phenolic hydroxides and ethers as chemical bonding agents.

To identify the possible sites of Cu(II) ions bonding to the cotton boll, FT-IR spectra were obtained for the cotton boll before and after Cu(II) adsorption, as shown in Figs. 6 and 7. Significant changes in the FT-IR spectra after the Cu(II) adsorption are found at the wave numbers of 3423, 3390, 1623, 1515, 1435–1252 and 1050 cm^{-1} .

Alcohols and amines display strong broad O–H and N–H stretching bands in the region $3400\text{--}3100 \text{ cm}^{-1}$ and N–H bending vibrations of amides appear in the region $1650\text{--}1590 \text{ cm}^{-1}$. The bands appear in the region $1515\text{--}1252$ and 1050 cm^{-1} indi-

Table 2

Comparison of the pseudo-first order and pseudo-second order reaction rate regression results

Initial concentration (mg l^{-1})	Reaction rate	Rate constant	Correlation coefficient
100	Pseudo-first order (per min)	2.7×10^{-3}	0.9366
120	Pseudo-first order (per min)	1.8×10^{-3}	0.9936
140	Pseudo-first order (per min)	1.7×10^{-3}	0.9979
160	Pseudo-first order (per min)	3.4×10^{-3}	0.8809
100	Pseudo-second order ($1 \text{ mg}^{-1} \text{ min}^{-1}$)	1.7×10^{-4}	0.9933
120	Pseudo-second order ($1 \text{ mg}^{-1} \text{ min}^{-1}$)	1.4×10^{-4}	0.9912
140	Pseudo-second order ($1 \text{ mg}^{-1} \text{ min}^{-1}$)	1.1×10^{-4}	0.9910
160	Pseudo-second order ($1 \text{ mg}^{-1} \text{ min}^{-1}$)	1.0×10^{-4}	0.9958

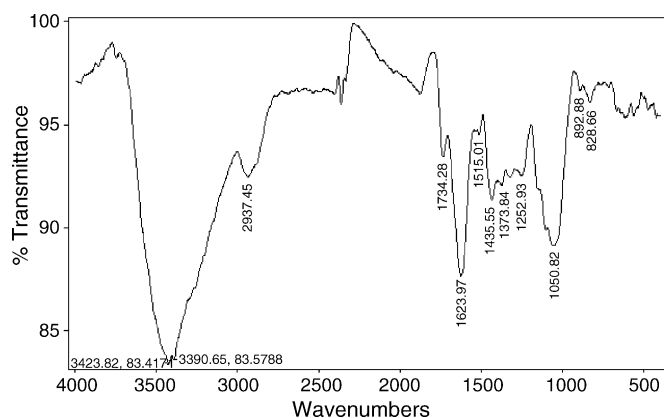


Fig. 6. FT-IR spectra of the cotton boll before Cu(II) adsorption.

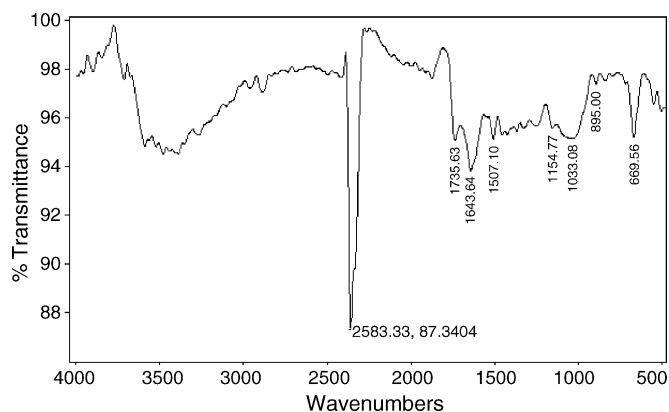


Fig. 7. FT-IR spectra of the cotton boll after Cu(II) adsorption.

cate $-\text{NO}_2$ groups of unsaturated compounds and C–O stretching vibrations of primer alcohols, respectively.

FT-IR results indicated that mainly oxygen atoms in the alcohol groups were involved in Cu(II) ions adsorption. Adsorption also affected all the chemical bonds with nitrogen atoms and nitrogen atoms in the amine and amide groups in cotton boll were involved in Cu(II) ions adsorption as well.

4. Conclusion

Batch adsorption studies showed that based on the Langmuir coefficients, the total capacity (monolayer saturation at equilibrium) of the cotton boll for Cu(II) ions was 11.40 mg g^{-1} . A comparison of the kinetic models on the overall adsorption

rate showed that the adsorption system was best described by the pseudo-second order rate model rather than by pseudo-first order rate model. Kinetic results of adsorption indicated that chemical sorption was the basic mechanism in this system. FT-IR results explained that mainly oxygen atoms in the alcohol groups and nitrogen atoms in the amine and amide groups in cotton boll were involved in Cu(II) ions adsorption.

Acknowledgements

The authors are grateful to the Ass. Prof. Murat Gizir for FT-IR analysis and reviewers for their helpful comments and suggestions.

References

- [1] N. Li, R. Bai, Copper adsorption on chitosan-cellulose hydrogel beads: behaviours and mechanisms, *Sep. Purif. Technol.* 42 (2005) 237–247.
- [2] A. Oztürk, T. Artan, A. Ayar, Biosorption of nickel(II) and copper(II) ions from aqueous solution by *Streptomyces coelicolor* A3(2), *Colloids Surf. B Biointerf.* 34 (2004) 105–111.
- [3] S. Rengaraj, Y. Kim, C.K. Joo, J. Yi, Removal of copper from aqueous solution by aminated and protonated mesoporous aluminas: kinetics and equilibrium, *J. Colloid Interf. Sci.* 273 (2004) 14–21.
- [4] A. Ozcan, A.S. Ozcan, S. Tunali, T. Akar, I. Kiran, Determination of the equilibrium, kinetic and thermodynamic parameters of adsorption of copper(II) ions onto seeds of capsicum annum, *J. Hazard. Mater.* B124 (2005) 200–208.
- [5] H.D. Ozsoy, H. Kumbur, Z. Özer, Adsorption of copper(II) ions to peanut hulls and *Pinus brutia* sawdust, *Int. J. Environ. Pollut.*, in press.
- [6] W. Ma, J.M. Tobin, Determination and modelling of effects of pH on peat biosorption of chromium, copper and cadmium, *Biochem. Eng. J.* 18 (2004) 33–40.
- [7] J. Hanzlik, J. Jehlicka, O. Sebek, Z. Weishauptova, V. Machovic, Multi-component adsorption of Ag(I), Cd(II) and Cu(II) by natural carbonaceous materials, *Water Res.* 38 (2004) 2178–2184.
- [8] V.K. Garg, R. Gupta, R. Kumar, R.K. Gupta, Adsorption of chromium from aqueous solution on treated sawdust, *Bioresour. Technol.* 92 (2004) 79–81.
- [9] K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani, S. Pattabhi, Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solution, *Bioresour. Technol.* 87 (2003) 129–132.
- [10] Ozer, D. Ozer, A. Ozer, The adsorption of copper(II) ions on to dehydrated wheat bran (DWB): determination of the equilibrium and thermodynamic parameters, *Process Biochem.* 39 (2004) 2183–2191.
- [11] Y.S. Ho, Pseudo-isotherms using a second order kinetic expression constant, *Adsorption* 10 (2004) 151–158.

- [12] B. Yu, Y. Zhang, A. Shukla, S.S. Shukla, K.L. Dorris, The removal of heavy metals from aqueous solutions by sawdust adsorption-removal of lead and comparison of its adsorption with copper, *J. Hazard. Mater.* B84 (2001) 83–94.
- [13] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, *Chem. Eng. J.* 70 (1998) 115–124.
- [14] K.G. Bhattacharyya, A. Sharma, Kinetics and thermodynamics of Methylene Blue adsorption on neem (*Azadirachta indica*) leaf powder, *Dyes Pigments* 65 (2005) 51–59.
- [15] Y.S. Ho, Effect of pH on lead removal from water using tree fern as the sorbent, *Bioresour. Technol.* 96 (2005) 1292–1296.
- [16] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, *Water Res.* 34 (3) (2000) 735–742.
- [17] A.K. Meena, G.K. Mishra, P.K. Rai, C. Rajagopal, P.N. Nagar, Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent, *J. Hazard. Mater.* B122 (2005) 161–170.
- [18] N. Basci, E. Kocadağistan, B. Kocadağistan, Biosorption of copper(II) from aqueous solutions by wheat shell, *Desalination* 164 (2004) 135–140.
- [19] S. Al-Asheh, F. Banat, R. Al-Omari, Z. Duvnjak, Prediction of binary sorption isotherms for the sorption of heavy metals by pine bark using single isotherm data, *Chemosphere* 41 (2000) 659–665.
- [20] V.K. Gupta, I. Ali, Utilisation of baggase fly ash (a sugar industry waste) for the removal of copper and zinc from wastewater, *Sep. Purif. Technol.* 18 (2000) 131–140.
- [21] Y.S. Ho, C.T. Huang, H.W. Huang, Equilibrium sorption isotherm for metal ions on tree fern, *Process Biochem.* 37 (2002) 1421–1430.
- [22] J.P. Chen, S. Wu, Simultaneous adsorption of copper ions and humic acid onto an activated carbon, *J. Colloid Interf. Sci.* 280 (2004) 334–342.
- [23] M.T. Veit, C.R.G. Tavares, S.M. Gomes-da-Costa, T.A. Guedes, Adsorption isotherms of copper(II) for two species of dead fungi biomasses, *Process Biochem.* 40 (2005) 3303–3308.